

101542822



Rec'd PST/PTO 20 JUL 2005

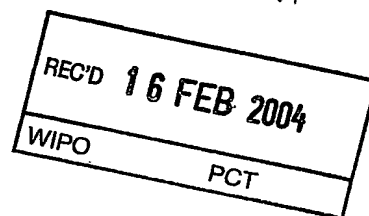
PCT/EP200 4/000359

Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

#2



Bescheinigung

Certificate

Attestation

Die angehefteten Unterla-
gen stimmen mit der
ursprünglich eingereichten
Fassung der auf dem näch-
sten Blatt bezeichneten
europäischen Patentanmel-
dung überein.

The attached documents
are exact copies of the
European patent application
described on the following
page, as originally filed.

Les documents fixés à
cette attestation sont
conformes à la version
initialement déposée de
la demande de brevet
européen spécifiée à la
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

03405032.8

**PRIORITY
DOCUMENT**
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Der Präsident des Europäischen Patentamts:
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk



Anmeldung Nr.:
Application no.: 03405032.8
Demande no:

Anmeldetag:
Date of filing: 24.01.03
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

Ciba Specialty Chemicals Holding Inc.
Klybeckstrasse 141
4057 Basel
SUISSE

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Crystalline modification of a manganese complex

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

C07C251/00

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

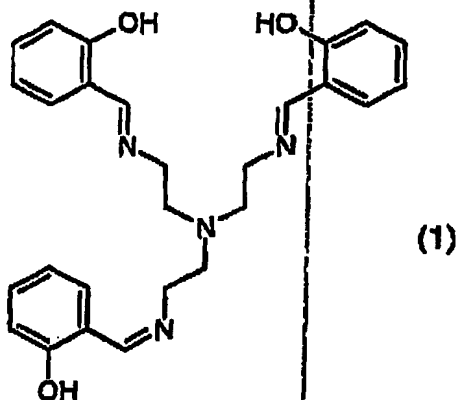
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL
PT SE SI SK TR LI

-1-

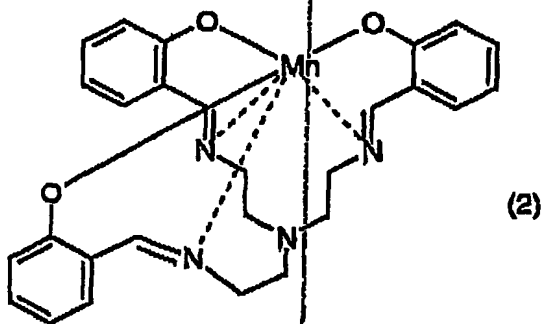
Crystalline Modification of a manganese complex

This invention relates to a novel polymorph crystal form of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine, a process for its preparation and the use thereof.

N,N',N''-tris[salicylideneaminoethyl]amine (saltren)



the 1:1 manganese(III) complex (Mn(III)saltren) thereof



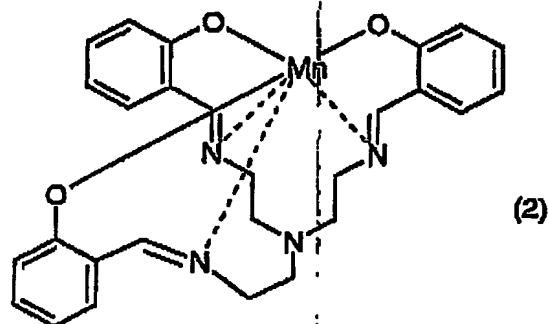
, its production as well as its use as peroxygen catalyst are known for example from WO0105925 (Examples 1 and 13), WO0109276 (Example 53) and WO02059245 (Example 15). The Mn(III) saltren compound has been known and producible as an amorph modification only.

The ability of a substance to exist in more than one crystal form is defined as polymorphism and these different crystal forms are named "polymorph modifications" or "polymorphs". In general, polymorphism is affected by the ability of a molecule of a substance to change its conformation or to form different intermolecular or intra-molecular interactions, particularly

hydrogen bonds, which is reflected in different atom arrangements in the crystal lattices of different polymorphs.

The different polymorphs of a substance possess different energies of the crystal lattice and, thus, in solid state they show different physical properties such as form, density, melting point, colour, stability, dissolution rate, milling facility, granulation, compacting etc.

Surprisingly a new crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine



, which is characterized by a peak at a d-spacing of about 6.87 Å in its powder X-ray diffraction pattern, has been found.

Specifically, the new crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)) is characterized by peaks with d-spacings of about 6.87 and 12.69 Å in its powder X-ray diffraction pattern.

More specifically, the new crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)) is characterized by peaks with d-spacings of about 3.51, 3.65, 4.20, 4.63, 4.95, 5.30, 6.38, 6.87, 7.50, 10.57 and 12.69 Å in its powder X-ray diffraction pattern.

Very specifically, the new crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)) is characterized by peaks with d-spacings of about 2.22, 2.48, 2.94, 3.14, 3.51, 3.65, 3.76, 3.94, 4.20, 4.63, 4.95, 5.30, 5.82, 6.19, 6.38, 6.87, 7.50, 8.59, 10.57 and 12.69 Å in its powder X-ray diffraction pattern.

The powder sample of the new crystal modification of Mn(III)saltren (compound (2)) has been analysed by a STOE-powder-diffractometer at room temperature (25°C) under Cu X-ray [$\lambda(\text{CuK}\alpha) = 1.540598 \text{ \AA}$].

Table 1 shows the characteristic spacing between the lattice planes designated by d and expressed in Angström units [\AA] and their corresponding characteristic relative intensity (weak, medium or strong).

Table 1

$d(\text{\AA})$	Intensity	$d(\text{\AA})$	Intensity
12.69	strong	4.63	medium
10.57	medium	4.20	medium
8.59	weak	3.94	weak
7.50	medium	3.76	weak
6.87	strong	3.65	medium
6.38	medium	3.51	medium
6.19	weak	3.14	weak
5.82	weak	2.94	weak
5.30	medium	2.48	weak
4.95	medium	2.22	weak

Fig. 1. shows the powder X-ray diffraction pattern of Mn(III)saltren (compound (2)), obtained from Example 1.

Fig.2. shows the powder X-ray diffraction pattern of Mn(III)saltren (compound (2)), obtained from Example 2.

In addition, by recording a single crystal of the new crystal modification of Mn(III)saltren (compound (2)) in a STOE Stadi 4-circle-diffractometer D045 under Mo X-rays [$\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$] at 293°K, there were obtained the basic crystallographic data for a single cell.

The size of the crystal has been 0.5mm x 0.35mm x 0.2mm

The basic crystallographic data (diffraction on single crystal), for the new crystal modification of Mn(III)saltren (compound (2)) are shown in Table 2.

Table 2

Crystal system	Monoclinic
Space group	P 2 ₁ /n
a[Å]	7.906
b[Å]	25.609
c[Å]	11.736
α [°]	90
β [°]	96.55
γ [°]	90
V[Å ³]	2360.6
Structure unit per cell (Z)	4
Absorption coefficient μ [mm ⁻¹]	0.597
F(000)	1064

In comparison to the amorph modification, the new crystal modification of Mn(III)saltren (compound (2)) has improved properties.

The new crystal modification posses for example improved formulation properties in comparison to the amorph modification. Further, the new crystal modification has an improved filterability.

The new crystal modification of Mn(III)saltren (compound (2)) can be used for improving the action of peroxides, for example in the treatment of textile material, without at the same time causing any appreciable damage to fibres and dyeings.

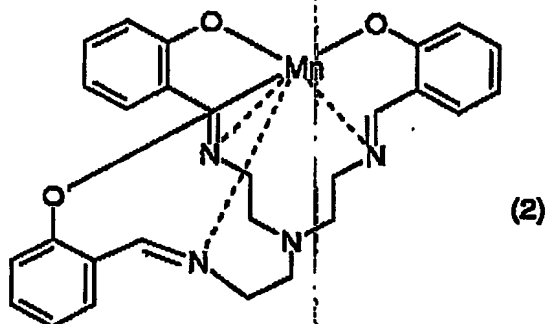
Peroxide-containing bleaching agents have been used in washing and cleaning processes for some time. They have an excellent action at a liquor temperature of 90°C and above, but their performance noticeably decreases with lower temperatures. It is known that various transition metal ions, added in the form of suitable salts, or coordination compounds containing such cations catalyse the decomposition of H₂O₂. In that way it is possible to increase the bleaching action of H₂O₂, or of precursors that release H₂O₂, or of other peroxo compounds, the bleaching action of which is unsatisfactory at lower temperatures.

Particularly significant for practical purposes are those combinations of transition metal ions and ligands the peroxide activation of which is manifested in an increased tendency towards

oxidation in respect of substrates and not only in a catalase-like disproportionation. The latter activation, which tends rather to be undesirable in the present case, could impair the bleaching effects of H_2O_2 and its derivatives which are insufficient at low temperatures.

In respect of H_2O_2 activation having effective bleaching action, mononuclear and polynuclear variants of manganese complexes with various ligands, especially with 1,4,7-trimethyl-1,4,7-triazacyclononane and optionally oxygen-containing bridge ligands, are currently regarded as being especially effective. Such catalysts have adequate stability under practical conditions and, with Mn^{III} , contain an ecologically acceptable metal cation, but their use is unfortunately associated with considerable damage to dyes and fibres.

The invention accordingly relates to the use of the new polymorph crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2))



as catalyst for oxidation reactions.

The new crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)) is preferably used together with peroxy compounds. Examples that may be mentioned in that regard include the following uses:

- a) the bleaching of spots or stains on textile material in the context of a washing process;
- b) the prevention of redeposition of migrating dyes during the washing of textile material;
- c) the cleaning of hard surfaces, especially wall tiles or floor tiles, more especially for removing mold stains;
- d) use in washing and cleaning solutions having an antibacterial action;
- e) as pretreatment agents for bleaching textiles;
- f) as catalysts in selective oxidation reactions in the context of organic synthesis.

A further use relates to the use of the new crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)) as catalyst for

reactions with peroxy compounds for bleaching in the context of paper-making. This relates especially to the bleaching of pulp, which can be carried out in accordance with customary processes. Also of interest is the use of the new crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylidene-aminoethyl]amine (compound (2)) as catalyst for reactions with peroxy compounds for the bleaching of waste printed paper.

Preference is given to the bleaching of spots or stains on textile material, the prevention of the redeposition of migrating dyes in the context of a washing process, or the cleaning of hard surfaces, especially wall or floor tiles.

It should be emphasised that the new crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)) does not cause any appreciable damage to fibres and dyeings, for example in the bleaching of textile material.

Processes for preventing the redeposition of migrating dyes in a washing liquor are usually carried out by adding to the washing liquor, which contains a peroxide-containing washing agent, the new crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)) in an amount of from 0.1 to 200 mg, preferably from 0.2 to 75 mg, especially from 0.2 to 30 mg, per litre of washing liquor. The new crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)) can be used together with other transition metal complexes. Such complexes are described for example in WO02088289, WO0105925, WO0109276, WO02059245, WO053574, EP902083 and EP955289.

The present invention relates also to a washing, cleaning, disinfecting or bleaching agent, containing

- I) 0 - 50 %, preferably 0 - 30 %, A) of an anionic surfactant and/or B) of a non-ionic surfactant,
- II) 0 - 70 %, preferably 0 - 50 %, C) of a builder substance,
- III) 1 - 99 %, preferably 1 - 70 %, D) of a peroxide or a peroxide-forming substance, and
- IV) E) the new crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)) in an amount which, in the liquor, gives a concentration of 0.2 - 50 mg/litre of liquor, preferably 0.2 - 30 mg/litre of liquor,

when from 0.2 to 20 g/litre of the washing, cleaning, disinfecting and bleaching agent are added to the liquor.

The above percentages are in each case percentages by weight, based on the total weight of the agent. The agents preferably contain from 0.005 to 2 % of the new crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)), especially from 0.01 to 1 % and preferably from 0.02 to 1 %.

When the agents according to the invention comprise a component A) and/or B), the amount thereof is preferably 1 - 50 %, especially 1 - 30 %.

When the agents according to the invention comprise a component C), the amount thereof is preferably 1 - 70 %, especially 1 - 50 %, Special preference is given to an amount of from 5 to 50 % and especially an amount of from 10 to 50 %.

Corresponding washing, cleaning, disinfecting or bleaching processes are usually carried out by using an aqueous liquor comprising a peroxide and from 0.1 to 200 mg of the new crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)) per litre of liquor. The liquor preferably contains from 0.2 to 30 mg of the compound of formula (2) per litre of liquor.

The agents according to the invention can be, for example, a peroxide-containing complete washing agent or a separate bleaching additive. A bleaching additive is used for removing coloured stains on textiles in a separate liquor before the clothes are washed with a bleach-free washing agent. A bleaching additive can also be used in a liquor together with a bleach-free washing agent.

The washing or cleaning agent according to the invention can be in solid or liquid form, for example in the form of a liquid, non-aqueous washing agent, comprising not more than 5 % by weight water, preferably comprising from 0 to 1 % by weight water, and, as base, a suspension of a builder substance in a non-ionic surfactant, e.g. as described in GB-A-2 158 454.

The washing or cleaning agent is preferably in the form of a powder or, especially, granules.

The latter can be prepared, for example, by first preparing an initial powder by spray-drying an aqueous suspension containing all the components listed above except for components D) and E), and then adding the dry components D) and E) and mixing everything together. It is also possible to add component E) to an aqueous suspension containing components A), B) and C), then to carry out spray-drying and then to mix component D) with the dry mass.

It is also possible to start with an aqueous suspension that contains components A) and C), but none or only some of component B). The suspension is spray-dried, then component E) is mixed with component B) and added, and then component D) is mixed in in the dry state.

It is also possible to mix all the components together in the dry state.

The anionic surfactant A) can be, for example, a sulfate, sulfonate or carboxylate surfactant or a mixture thereof. Preferred sulfates are those having from 12 to 22 carbon atoms in the alkyl radical, optionally in combination with alkyl ethoxysulfates in which the alkyl radical has from 10 to 20 carbon atoms.

Preferred sulfonates are e.g. alkylbenzenesulfonates having from 9 to 15 carbon atoms in the alkyl radical. The cation in the case of anionic surfactants is preferably an alkali metal cation, especially sodium.

Preferred carboxylates are alkali metal sarcosinates of formula $R-CO-N(R^1)-CH_2COOM^1$ wherein R is alkyl or alkenyl having from 8 to 18 carbon atoms in the alkyl or alkenyl radical, R^1 is C_1-C_4 alkyl and M^1 is an alkali metal.

The non-ionic surfactant B) can be, for example, a condensation product of from 3 to 8 mol of ethylene oxide with 1 mol of a primary alcohol having from 9 to 15 carbon atoms.

As builder substance C) there come into consideration, for example, alkali metal phosphates, especially tripolyphosphates, carbonates or hydrogen carbonates, especially their sodium salts, silicates, aluminosilicates, polycarboxylates, polycarboxylic acids, organic phosphonates, aminoalkylenepoly(alkylene-phosphonates) or mixtures of those compounds.

Especially suitable silicates are sodium salts of crystalline layered silicates of the formula $\text{NaHSi}_t\text{O}_{2t+1} \cdot p\text{H}_2\text{O}$ or $\text{Na}_2\text{Si}_t\text{O}_{2t+1} \cdot p\text{H}_2\text{O}$ wherein t is a number from 1.9 to 4 and p is a number from 0 to 20.

Among the aluminosilicates, preference is given to those commercially available under the names zeolite A, B, X and HS, and also to mixtures comprising two or more of those components.

Among the polycarboxylates, preference is given to polyhydroxycarboxylates, especially citrates, and acrylates and also copolymers thereof with maleic anhydride. Preferred polycarboxylic acids are nitrilotriacetic acid, ethylenediamine-tetraacetic acid and ethylenediamine disuccinate either in racemic form or in the enantiomerically pure (S,S) form.

Phosphonates or aminoalkylenepoly(alkylenephosphonates) that are especially suitable are alkali metal salts of 1-hydroxyethane-1,1-diphosphonic acid, nitrilotris(methylenephosphonic acid), ethylenediaminetetramethylenephosphonic acid and diethylenetriamepentamethylenephosphonic acid.

As the peroxide component D) there come into consideration, for example, the organic and inorganic peroxides known in the literature and available commercially that bleach textile materials at conventional washing temperatures, for example at from 10 to 95°C.

The organic peroxides are, for example, mono- or poly-peroxides, especially organic peracids or salts thereof, such as phthalimidoperoxycaproic acid, peroxybenzoic acid, diperoxydodecanedioic acid, diperoxynonanedioic acid, diperoxydecanedioic acid, diperoxyphthalic acid or salts thereof.

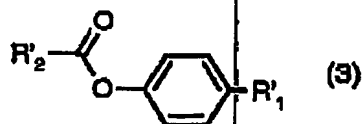
Preferably, however, inorganic peroxides are used, for example persulfates, perborates, percarbonates and/or persilicates. It will be understood that mixtures of inorganic and/or organic peroxides can also be used. The peroxides may be in a variety of crystalline forms and have different water contents, and they may also be used together with other inorganic or organic compounds in order to improve their storage stability.

The peroxides are added to the agent preferably by mixing the components, for example using a screw metering system and/or a fluidised bed mixer.

The agents may comprise, in addition to the combination according to the invention, one or more optical brighteners, for example from the class bis-triazinylamino-stilbenedisulfonic acid, bis-triazolyl-stilbenedisulfonic acid, bis-styryl-biphenyl or bis-benzofuranylbiphenyl, a bis-benzoxalyl derivative, bis-benzimidazolyl derivative or coumarin derivative or a pyrazoline derivative.

The agent may also comprise suspending agents for dirt, e.g. sodium carboxymethylcellulose, pH regulators, e.g. alkali metal or alkaline earth metal silicates, foam regulators, e.g. soap, salts for regulating the spray-drying and the granulating properties, e.g. sodium sulfate, perfumes and, optionally, antistatic agents and softeners, enzymes, such as amylase, bleaches, pigments and/or toning agents. Such constituents must especially be stable towards the bleaching agent used.

In addition to the inventive bleach catalyst (compound (2)) it is also possible to use further transition metal salts or complexes known as bleach-activating active ingredients and/or conventional bleach activators, that is to say compounds that, under perhydrolysis conditions, yield unsubstituted or substituted perbenzo- and/or peroxy-carboxylic acids having from 1 to 10 carbon atoms, especially from 2 to 4 carbon atoms. Suitable bleach activators include the customary bleach activators, mentioned at the beginning, that carry O- and/or N-acyl groups having the indicated number of carbon atoms and/or unsubstituted or substituted benzoyl groups. Preference is given to polyacylated alkylenediamines, especially tetraacetylenediamine (TAED), acylated glycolurils, especially tetraacetylglycoluril (TAGU), N,N-diacetyl-N,N-dimethylurea (DDU), acylated triazine derivatives, especially 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), compounds of formula (3):



wherein R₁ is a sulfonate group, a carboxylic acid group or a carboxylate group, and wherein R₂ is linear or branched (C₇-C₁₅)alkyl, especially activators known under the names SNOBS, SLOBS and DOBA, acylated polyhydric alcohols, especially triacetin, ethylene glycol diacetate and 2,5-diacetoxy-2,5-dihydrofuran, and also acetylated sorbitol and mannitol and

acylated sugar derivatives, especially pentaacetylglucose (PAG), sucrose polyacetate (SUPA), pentaacetylfructose, tetraacetylxylose and octaacetylactose as well as acetylated, optionally N-alkylated glucamine and gluconolactone. It is also possible to use the combinations of conventional bleach activators known from German Patent Application DE-A-44 43 177. Nitrile compounds that form perimline acids with peroxides also come into consideration as bleach activators.

Further preferred additives to the agents according to the invention are polymers which, during the washing of textiles, prevent staining caused by dyes in the washing liquor that have been released from the textiles under the washing conditions. Such polymers are preferably polyvinylpyrrolidones or polyvinylpyridine-N-oxides which may have been modified by the incorporation of anionic or cationic substituents, especially those having a molecular weight in the range of from 5000 to 60 000, more especially from 10 000 to 50 000. Such polymers are preferably used in an amount of from 0.05 to 5 % by weight, especially from 0.2 to 1.7 % by weight, based on the total weight of the washing agent.

It is possible to add the new crystal modification of compound 2 to the washing, cleaning, disinfecting or bleaching agent in the form of preformed granules, containing 1-40 % of the new crystal modification of compound 2.

The new crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylidene-aminoethyl]amine (compound (2)) also exhibit a markedly improved bleach-catalysing action on coloured stains on hard surfaces. The compounds are also very suitable for cleaning hard surfaces at low temperatures.

The use of the new crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)) as catalyst for reactions with peroxy compounds in cleaning solutions for hard surfaces, especially wall or floor tiles, is therefore of special interest.

The new crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylidene-aminoethyl]amine (compound (2)), also has together with peroxy compounds, excellent antibacterial action. The use of the new crystal modification of the 1:1 manganese (III)

complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)) for killing bacteria or for protecting against bacterial attack is therefore likewise of interest.

The new crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylidene-aminoethyl]amine (compound (2)) is also outstandingly suitable for selective oxidation in the context of organic synthesis, especially the oxidation of organic molecules, e.g. of olefins to form epoxides. Such selective transformation reactions are required especially in process chemistry. The invention accordingly relates also to the use of the new crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)) in selective oxidation reactions in the context of organic synthesis.

The new crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylidene-aminoethyl]amine (compound (2)) is obtainable by

- a) adding a solution comprising 3 parts of salicylaldehyd and 1 part of tris-(2-aminoethyl) amine to a Mn(III) solution, which can optionally comprise some amount of a base, such as NaOH, KOH, etc., and
- b) isolation and purification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)).

Suitable organic solvents for step a) are DMF, N-methylpyrrolidone, Dimethylsulfoxide or alcohols such as methanol, ethanol, butanol etc...

The reaction temperature for step a) are preferably between 15 – 50°C, more preferably between 20 – 40°C, most preferably room temperature (25°C).

The isolation and purification (step b) is done by conventional means. Preferably, the compound is filtrated, washed with some amount of the solvent and dried in vacuum.

The present invention is illustrated but in no way limited by the following examples.

Example 1

To an ethanolic solution containing 3 parts of salicylaldehyd, 1 part of tris-(2-aminoethyl)-amine and 2 equivalents of a NaOH-solution (50%), which has been stirred at 25°C, a stocheometric amount of an ethanolic Mn(III)salt solution is added. The Mn(III)saltren with new crystal form is obtained after a few minutes. The precipitated compound is filtered off, washed and dried in vacuum.

Example 2

3 parts of salicylaldehyde and 1 part of tris-(2-aminoethyl)amine are solved in DMF. This solution is stirred for 20h at a temperature of 25°C. Afterwards, the Mn(III)salt solved in DMF is added. Simultaneously, 1 wt-% of a Mn(III)saltren seed crystal, obtainable according to Example 1 is also added to the solution. The Mn(III)saltren with new crystal form is obtained after a few minutes. The precipitated compound is filtered off, washed and dried in vacuum.

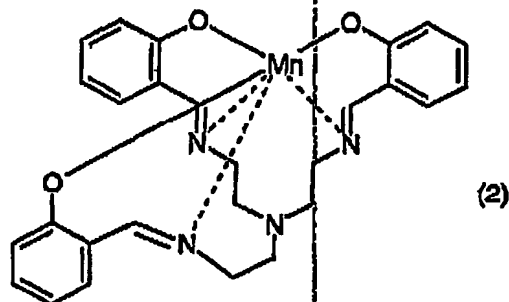
Brief description of the drawings:

Fig.1: shows the X- Fig. 1. shows the powder X-ray diffraction pattern of Mn(III)saltren (compound (2)), obtained from Example 1. The powder sample of the new crystal modification of Mn(III)saltren (compound (2)) has been analysed by a STOE-powder-diffractometer at room temperature (25°C) under Cu X-ray [$\lambda(\text{CuK}\alpha) = 1.540598 \text{ \AA}$].

Fig.2. shows the powder X-ray diffraction pattern of Mn(III)saltren (compound (2)), obtained from Example 2. The powder sample of the new crystal modification of Mn(III)saltren (compound (2)) has been analysed by a STOE-powder-diffractometer at room temperature (25°C) under Cu X-ray [$\lambda(\text{CuK}\alpha) = 1.540598 \text{ \AA}$].

CLAIMS

1. A crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine



characterized by a peak at a d-spacing of about 6.87 Å in its powder X-ray diffraction pattern.

2. A crystal modification of 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)) characterized by peaks at d-spacings of about 6.87 and 12.69 Å in its powder X-ray diffraction pattern

3. A crystal modification of 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)) characterized by peaks at d-spacings of about 3.51, 3.65, 4.20, 4.63, 4.95, 5.30, 6.38, 6.87, 7.50, 10.57 and 12.69 Å in its powder X-ray diffraction pattern

4. A crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)) characterized by peaks at d-spacings of about 2.22, 2.48, 2.94, 3.14, 3.51, 3.65, 3.76, 3.94, 4.20, 4.63, 4.95, 5.30, 5.82, 6.19, 6.38, 6.87, 7.50, 8.59, 10.57 and 12.69 Å in its powder X-ray diffraction pattern.

5. A crystal modification of 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)), which has a characteristic X-ray powder pattern obtained by X-ray diffraction on a powder sample of the new crystal modification in the instrument STOE-powder-diffractometer at room temperature (25°C) under Cu X-ray [$\lambda(\text{CuK}\alpha) = 1.540598 \text{ Å}$] represented by the following spacings between lattice planes:

d(Å)	Intensity	d(Å)	Intensity
12.69	strong	4.63	medium
10.57	medium	4.20	medium
8.59	weak	3.94	weak
7.50	medium	3.76	weak
6.87	strong	3.65	medium
6.38	medium	3.51	medium
6.19	weak	3.14	weak
5.82	weak	2.94	weak
5.30	medium	2.48	weak
4.95	medium	2.22	weak

6. A crystal modification of 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)) according to any one of the preceeding claims, characterized in that in accordance with X-ray diffraction on its sample single crystal it is represented by the following basis crystallographic data:

Crystal system	monoclinic
Space group	P 2 ₁ /n
a[Å]	7.906
b[Å]	25.609
c[Å]	11.736
α [°]	90
β [°]	96.55
γ [°]	90
V[Å ³]	2360.6
Structure unit per cell (Z)	4
Absorption coefficient μ [mm ⁻¹]	0.597
F(000)	1064

7. Use of the crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)) according to any one of the preceeding claims as catalyst for oxidation reactions.

8. Use according to claim 7, wherein the crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine is used in a washing, cleaning, disinfecting or bleaching agent.

9. Use according to claims 7 or 8, wherein the crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine is used together with a peroxy compound for the bleaching of spots or stains on textile material or for the prevention of the redeposition of migrating dyes in the context of a washing process of textile materials or for the cleaning of hard surfaces.

10. Use according to claims 7 or 8, wherein the crystal modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine according to claims 1 - 6 is used as a catalyst for reactions with a peroxy compound for bleaching in the context of paper-making.

11. A washing, cleaning, disinfecting or bleaching agent, containing

I) 0 - 50 %, A) of an anionic surfactant and/or B) of a non-ionic surfactant,

II) 0 - 70 %, C) of a builder substance,

III) 1 - 99 %, D) of a peroxide or a peroxide-forming substance, and

IV) E) the crystal modification of the 1:1 manganese (III) complex of N,N',N''-Tris[salicylideneaminoethyl]amine (compound (2)) according to claims 1 - 6 in an amount which, in the liquor, gives a concentration of 0.2 - 50 mg/litre of liquor, when from 0.2 to 20 g/litre of the washing, cleaning, disinfecting and bleaching agent are added to the liquor,

12. Process for the preparation of the modification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)) according to Claims 1 - 6 by
a) adding a solution comprising 3 parts of salicylaldehyd and 1 part of tris-(2-aminoethyl)amine to a Mn(III) solution, which can optionally comprise some amount of a base, and

b) isolation and purification of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine (compound (2)),

Abstract

This invention relates to a novel crystal form of the 1:1 manganese (III) complex of N,N',N''-tris[salicylideneaminoethyl]amine, a process for its preparation and the use thereof.

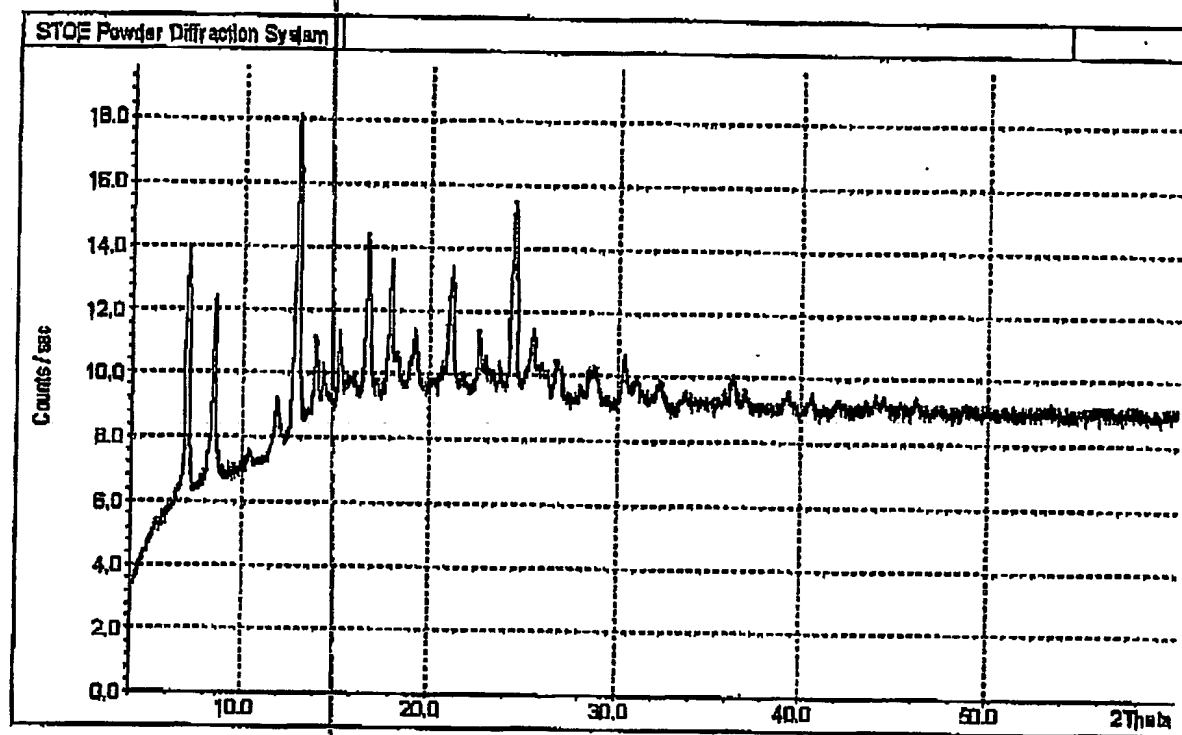


Fig-1: powder X-ray diffraction pattern of Mn(II)salicylate (compound (2)), obtained from Example 1.

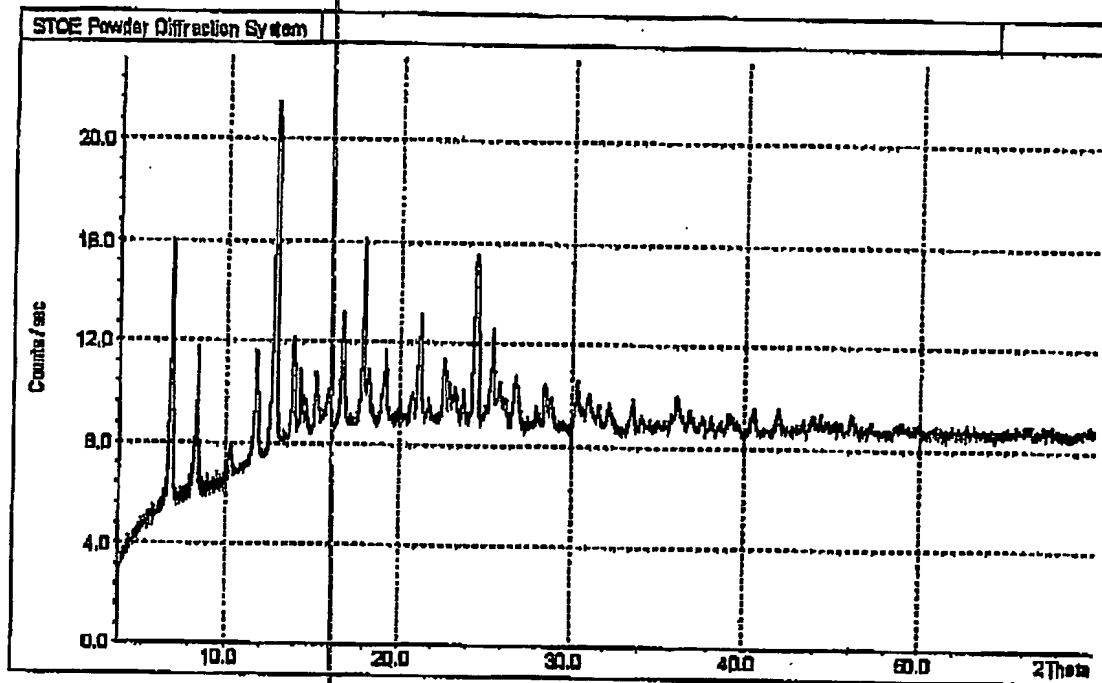


Fig.2.: powder X-ray diffraction pattern of Mn(III)salen (compound (2)), obtained from Example 2

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.